

ACIDIC DEPOSITION TO A NATURAL SNOW SURFACE

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Abstract

Bulk atmospheric deposition was sampled over a one-year interval (July 1984-June 1985) in a forested watershed in the Central Rockies of Colorado (2900 m). The total annual bulk deposition was as follows: ($\text{mg}/\text{m}^2/\text{wk}$): calcium, 5.6; magnesium, 0.82; sodium, 4.6; potassium, 2.3; sulfate, 24.7; nitrate nitrogen 4.5; chloride 1.8; ammonium nitrogen, 3.2; total particulate material 121; hydrogen ion 0.19; soluble reactive phosphorus, 0.065; total soluble phosphorus, 0.125; particulate phosphorus, 0.24; total soluble nitrogen, 9.6. The median pH over the entire year was 5.0, and the minimum pH was 4.2. The bulk deposition for all constituents during the snow season (November-March) was compared with the annual bulk deposition. During the snow season, deposition rate was lower for all constituents. Lower deposition rates for most constituents was partly explained by the smaller amount of wet precipitation in the winter (6.4 mm/wk; annual average 11.7 mm/wk). However, potassium, ammonium, and phosphorus fractions were disproportionately low during the snow season.

Dry deposition to the snow surface was estimated by two independent methods. First, on 11 different dates, the composition of snow on a snow platform was determined quantitatively at the beginning and the end of a sampling interval during which no further snowfall occurred. A second estimate was derived from measurements of the amount and chemistry of fresh snow as compared with the amount and chemistry of bulk deposition during the entire snow season. The two types of estimates agreed very well for sulfate and nitrate, representing sulfur and nitrogen oxides, and for ammonium. The mean of these two separate estimates was taken as a quantitative estimate of the rate of dry deposition to the snow surface; for sulfate the rate was 9.9

mg/m²/wk and for nitrate nitrogen it was 0.85 mg/m²/wk. On this basis, it was calculated that dry deposition of sulfate on snow was 17% of the annual deposition and 63% of the winter deposition of sulfur oxides. Dry deposition of nitrogen oxides on snow accounted for 8% of the annual total deposition and 42% of the deposition during the snow season. Estimates were also made for the major metal cations, for ammonium, and for chloride.

An extraction device of new design was used in measuring the total amounts of the sulfur and nitrogen oxides present in the atmosphere at the sampling site over intervals of 3-4 days on 11 occasions during the snow season. The extraction device showed evidence of good performance as judged by efficiency of recovery in serially arranged extraction units, good general agreement of observed concentrations of sulfur and nitrogen oxides with concentration measured independently in the past by gas phase analysis, and conformance of the computed sedimentation velocities with expected values from the literature. The average sedimentation velocity for sulfur oxides on snow over the snow season was 1.0 cm/sec; the average for nitrogen oxides was 0.76 cm/sec. Concentrations of sulfur oxides, including all chemical species, averaged 255 pptv; nitrogen oxides averaged 209 pptv. The extraction device appears to be highly suitable for ecologically oriented investigations in which the primary emphasis is on the quantification of total nitrogen and sulfur oxides.

Introduction

It is now well known that the combustion of fossil fuels is accompanied by the release of insufficient amounts of nitrogen and sulfur oxides to affect the chemistry of the atmosphere in densely populated regions (NRC 1983). Furthermore, it is known that the conversion of these oxides to strong mineral acids in the presence of water, and the resulting acidification of atmospheric deposition, can have important environmental effects, including the acidification of poorly buffered surface waters (Haines 1983) and possibly direct damage to terrestrial vegetation where acidification is most extreme. However, the importance and extent of these phenomena has been widely recognized for only a little more than a decade. Thus many of the mechanisms that control the deposition of acidic materials, that affect the transmission of acidic materials through ecosystems, and that govern the effects of the resulting chemical changes on organisms and on the geochemistry of soils and fresh waters are as yet very poorly understood.

It is standard practice to measure atmospheric deposition by means of collectors, some of which are designed to remain open continuously and some to remain open only when there is rain or snow (Galloway and Likens 1976). While the use of such collectors provides a standardized measure of deposition that can be used for the comparison of sites, it is not possible to assume with confidence that deposition on ecosystem surfaces will be accurately reflected by the deposition of materials on a collecting surface. Natural surfaces within ecosystems are extremely varied, and may differ importantly from collectors in texture, surface area, porosity, and other factors that affect deposition. Thus the properties of natural surfaces as collectors of atmospheric materials must be studied directly if the data from standardized

collectors are to be converted into estimates of actual transport from the atmosphere to natural surfaces.

It should be possible, given specific atmospheric conditions, to define empirically a transfer coefficient that would describe the movement of an atmospheric constituent to an environmental surface. If studies of this type were extended over a wide range of atmospheric conditions, over a wide range of environmental surfaces, and over a wide range of atmospheric constituents, there would be a solid basis for the prediction of deposition on natural surfaces. While work of this type has been done (Hicks 1984, Pruppacher et al. 1983), specific transfer functions, which typically take the form of sedimentation velocities, are as yet not well defined for natural surfaces, and are more often modeled than measured (Slinn 1982). While the range of possible substrates and conditions is very great, some combinations are especially important because of their frequent occurrence. In the Central Rockies, and in many other locations where acidic deposition is a matter for concern, terrestrial surfaces are covered with snow for large portions of the year. The rate at which these snow surfaces accumulate atmospheric materials, and particularly nitrogen and sulfur oxides and their derivatives, is therefore of great interest in view of the constant contact of snow surfaces with air masses containing these oxides.

The purpose of this study was to determine the rates at which snow surfaces at a mountain location in the Central Rockies accumulate nitrogen and sulfur oxides as a result of dry deposition from the atmosphere, and the comparison of these rates with the rates of annual and seasonal bulk deposition.

Study Site

The study was conducted at the Como Creek watershed in Boulder County, Colorado, at an elevation of 2900 m (Figure 1). This site is 80% forested with conifers and aspen and receives annual mean wet precipitation of about 600 mm. Past studies at this site have shown that significant deposition of strong mineral acids occurs throughout the year, and that there is a trend across years toward greater deposition of strong mineral acids (Lewis and Grant 1980, Grant and Lewis 1982). Furthermore, studies of atmospheric chemistry have shown that there are frequent upslope movements of air from the urban corridor to the east, and that these movements bring with them urban pollutants including nitrogen oxides, sulfur oxides, and ozone (Fehsenfeld et al. 1983, Huebert et al. 1982). However, the site is also affected by more generalized sources of nitrogen and sulfur oxides associated with power production, whose influence can be seen throughout the montane regions of Colorado (Lewis et al. 1984). Strictly local sources of air pollution are very minor; the surrounding area is sparsely populated.

Methods

Samples were taken weekly between July 1984 and June 1985 from a bulk collector; this provided a continuous estimate of the total atmospheric deposition to a standard collecting surface throughout the study year. The bulk collector was identical to collectors that have been used in previous studies at the same site, and is described in detail elsewhere (Figure 2: Lewis and Grant 1978). The collector consists of an inverted plexiglas pyramid with a collecting area of 0.23 m^2 , which is sufficiently large to allow the analysis of a large suite of constituents even in dry deposition

collected over a single week. With respect to wet precipitation, the properties of the collector are very similar to those of a standard rain gauge (Grant and Lewis 1982).

The plexiglas surface of the collector is mounted over an insulated box that contains a thermostatically-controlled heat source. During winter, this heat source keeps the plexiglas surface sufficiently warm to melt snow. This prevents the snow from accumulating and being blown away, as would occur easily at this site because of the very dry winter weather. Inside the collector, the melted snow or summer rain accumulates in a hard glass receiving vessel after passing through a vapor barrier that prevents evaporation. The tubing and collecting vessel are cleaned and replaced weekly.

Each time a bulk deposition sample was collected, the collecting surface was rinsed with a measured portion of deionized water. Corrections were later made for the added volume and reduced concentrations of dissolved substances resulting from the addition of this water. The amount of water added was typically a small percentage of the total volume of the sample (5-15%). However, in a few instances the amount of wet precipitation was nil or very small. In these instances, the rinse water was added as usual and a complete set of analyses was done on the rinse water.

Samples were analyzed for a full suite of major ionic materials. However, the greatest emphasis will be placed here on substances that can be tracked between the air mass and the site of deposition, and particularly on nitrogen and sulfur oxides, which are associated with strong acidity.

The pH of all wet precipitation samples was determined immediately after collection with a Fisher Accumet pH meter checked against two buffer solutions

with appropriate precautions for the protection of weakly buffered samples (cf. Lewis et al. 1984). The remainder of the sample was filtered through preweighed glass fiber paper (Whatman GF/C, pore size 0.7 μ m) that was then reweighed after it had been dried to constant weight at 60°C.

One portion of the filtered sample was treated with cesium chloride to make a concentration of 1000 ppm and with lanthanum oxide to make 10,000 ppm in sufficient HCl to depress the pH of the subsample to 2.0 or less. Atomic absorption analysis was done for the four major metal cations (sodium, potassium, calcium, magnesium). Blanks, standards, replicates, and spikes were run routinely to assure appropriate precision and accuracy.

A second portion of the filtered sample was used for ion chromatography (Dionex Model 2110 ion chromatograph). The samples were analyzed for chloride, nitrate, nitrite, and sulfate. Analyses were accompanied by the use of duplicates, spikes, standards, and blanks.

Ammonium, soluble reactive phosphorus, total soluble phosphorus, particulate phosphorus, and total nitrogen were analyzed spectrophotometrically. The methods were as follows: phenolhypochlorite for ammonium (Grasshoff 1976), acid molybdate for reactive phosphorus (Murphy and Riley 1962), persulfate digestion followed by acid molybdate for total soluble phosphorus, pyrolysis for particulate phosphorus (Solorzano and Sharp 1980a), and persulfate digestion for total N (Valderrama 1981).

The design of the study required that snow be collected quantitatively in an area where the snow would not be falling through a tree canopy. At the same time, natural shielding by vegetation was also required. For these reasons, a natural clearing measuring approximately 50 m in diameter was chosen as a collecting site. This clearing was surrounded by aspen and

conifers and was covered with natural grasses and some exposed rock. Within the center of this clearing, a platform was erected for the collection of snow. The platform consisted of four corner posts forming a square 2.44 meters on each side. A frame consisting of pine 2 x 4s was constructed within this square. The frame was constructed in such a way that it could be supported by the four corner posts but at the same time could also be moved up and down to accommodate changes in snow cover. The frame was covered with plywood, and the plywood was in turn covered with inert plastic sheet. The platform was allowed to sit 20 cm above the surface of the snowpack. Prior to the collection of snow, the collecting surface was cleaned of snow and of other deposits.

The inert surface of the snow collector was allowed to collect snow through an entire snowfall episode. At the end of the snowfall, the snow was sampled by methods outlined below and the snow type and depth were determined. A fresh snowfall followed by a collection of this type marked the start of an interval over which changes in snow chemistry under the influence of dry atmospheric deposition could be studied.

Ideal conditions for the study of changes in snow chemistry under the influence of dry atmospheric deposition would include an unmoving fresh snow cover that remains intact for a period of 3 to 5 days, after which time it could be sampled so that the changes in total inventory of materials in the snow could be determined. The rate of dry deposition to the snow surface could thus be calculated. A number of ideal sampling intervals of this type occurred during the course of the study. In numerous other instances, however, conditions departed from the ideal and in some instances these departures were so great that the second set of samples could not be

considered suitable for comparison with the first set of samples taken over a sampling interval. The first and last weeks of the snowfall season sometimes coincided with rises in daytime temperature that were sufficient to cause melting of the snow from the bottom. This caused the materials in the snow to be lost from the collector in the form of runoff. In other instances, the amount of wind was so great during the sampling interval that the initial snow cover was disturbed or snow was moved onto the collecting surface from other sites. The melting of snow or the movement of snow through the air prevented valid comparisons of the inventory of atmospheric materials in snow at the beginning and at the end of the sampling interval.

In some instances, small amounts of additional snow fell during the sampling interval. In these cases, it was considered possible, at least from the theoretical point of view, to add the contributions of any additional snow to the original contribution at the beginning of the sampling interval and thus still obtain estimates of the deposition of materials from a dry atmosphere onto the snow surface. Thus although data for such sampling intervals are not ideal due to the added source of variation, an attempt was made to use them as well as the data for the more ideal intervals over which no snow or wind interference occurred.

At the beginning of each snow sampling interval, a maximum-minimum thermometer was mounted on one of the support posts near the snow cover but away from direct sunlight. The maximum-minimum temperatures were recorded over the course of the sampling interval. In addition, an anemometer was mounted 2 meters above the snowpack and the totalized wind passing the snow sampler over the sampling interval was determined on the basis of the anemometer readings.

When the initial samples of fresh snow were taken, a determination was made in the field of snow type. Six cores of snow were then removed from the collecting surface with a round, inert coring device (134 mm diameter). The depth of the snow was measured each time a core was taken and these numbers were averaged to produce an estimate of the average snow depth. The snow cores were combined in a single container and were allowed to melt at room temperature immediately after collection. The water equivalent of the snow was then measured and this information was used later for computations of snow density. The liquid sample was then taken to the analytical laboratory in Boulder, 45 minutes distant from the collection site. The samples were processed immediately upon their arrival at the laboratory by a protocol like that described above for bulk precipitation. The procedures for snow sampling were repeated at the end of each snow sampling interval.

Air samples were taken continuously at the snow collection site over each sampling interval. The continuous sampling of air was accomplished by means of an extraction device of new design based on the water solubility of nitrogen and sulfur oxides and the hydrated forms of these oxides. The extraction apparatus consisted of 4 inert plastic tubes 2 meters tall and 22 mm in diameter (Figure 3). Each of these tubes was fitted at each end with a cap bearing a spout 6 mm in diameter. In addition, a perforated plate was mounted permanently 7 cm from the bottom of each tube. The perforations, which were designed to disperse air flow through the tubes, were 1 mm in diameter. A shunt, consisting of inert flexible hose, was placed around the perforated plate. The shunt was closed by a pinch clamp when the tubes were in use, but was opened for draining of the tubes.

The extraction tubes were joined in series with inert hose; hose leaving the top of one extraction tube led to the bottom of the next tube. The hose entering the bottom of the first tube in the series was the entry point to the extraction tube series and the hose leaving the top of the last tube in the series was the exit point from the series. A large vacuum pump on the outlet side of the series drew a steady flow of air through the series of four tubes when the extractor was in operation.

Whenever the extraction unit was to be used, each of the four tubes was filled to slightly above half capacity with a measured amount (300 ml) of deionized water. At the same time, tubes identical to those used in the extractor were filled to the same level with the same deionized water so that a field blank would be available for the extractor. At the start of an extraction run, the vacuum pump was turned on, causing air to enter the bottom of the first extraction tube and then to pass in series from the bottom to the top of each tube, and finally to be exhausted through the pump. The rate of air flow was measured on the intake side at the start and at the end of each extraction interval. The extraction interval was coincident with the snow deposition sampling interval.

At the end of each extraction interval, the pump was shut off and each tube was drained separately. The draining of each tube was done through the supply hose to that particular tube, and thus removed any atmospheric material that might have accumulated on the air intake to any given extraction tube. The amount of water in each tube, which was frequently less than the initial amount due to losses from evaporation, was measured at the time the tube was emptied.

Chemical analysis of the water from the extraction tube focused on nitrogen and sulfur oxides. The amounts of nitrate and nitrite in the water of the extraction tubes were considered to have originated from nitrogen oxides in gaseous form or from the mineral acid derivatives of these oxides in the atmosphere. Similarly, sulfate in the tubes was considered to have been derived from sulfur oxides or from sulfuric acid in the atmosphere. Thus the measurement of minute amounts of nitrate, nitrite, and sulfate was essential to the interpretation of the extractions. Analysis of very small amounts of these ions is practical for samples of small volume only by the use of ion chromatography. Furthermore, standard ion chromatography configurations are not suitable; the use of an extraction column capable of accumulating the ion content of 10-25 ml of sample is required in addition to the use of standard separator columns. Given the use of such concentrator columns in conjunction with standard separator columns, the amounts of nitrite, nitrate, and sulfate that can be measured are about 1 ug/l, but the actual limits for a particular run depend largely on the blanks.

It is assumed that extraction of the air stream passing through any given tube may not be 100% efficient. For a given atmospheric constituent, solubility and contact time are essentially the same from one tube to the next. Thus for a given constituent, the amount of an extraction product will form a decreasing exponential series, the extrapolation of which will indicate the amount of the constituent in the air entering the system.

Results

Bulk Deposition

Table 1 summarizes the chemical composition of bulk precipitation in terms of concentration. As expected, concentrations are extremely variable. This is explained not only by the variation in atmospheric characteristics at the site, but, even more importantly, by the varying amounts of wet precipitation. Wet precipitation occurred on all weeks of the one-year study period except one (20-26 November, 1984). However, on a few dates the amounts of wet precipitation were very small. When the volume of wet precipitation is very small, dry deposition strongly affects the concentrations. On the week when there was no wet precipitation, a dummy value of 0.01 liters for the wet precipitation was used so that a concentration value could be carried through to the stage at which deposition rates were calculated, at which point the volume of wet precipitation is factored out. Concentrations for this dummy volume are of course quite high, as they represent the concentration of all the dry deposition from an entire week concentrated in a water volume of only 10 ml. The same principle applies when the amount of wet precipitation was measurable but small. For example, on the week of 14 January, the amount of wet precipitation was 20 ml for the collector. The concentrations of materials on this week were quite high, as would be expected due to the concentration of the dry deposition for the week being concentrated in such a small volume of water. Even when the amounts of wet precipitation are larger, the amount of wet precipitation governs the relative influence of dry deposition on the concentrations reported in the table. In addition, wet precipitation tends to change the balance between constituents because moisture in the air will more readily remove some constituents than others.

For all of these reasons, the individual concentration values for precipitation samples are not easily interpreted. It is worth noting, however, that the pH values for undiluted samples (i.e., excluding the four samples for which dilution had to be done because of small sample volumes) had a median value of 5.0 and a minimum value of 4.2.

Table 2 summarizes the weekly deposition rates. Although these have a smaller range of variation than the concentrations, they are still subject to variation associated with the amount of wet precipitation, which affects the efficiency of removal of materials from the atmosphere.

Table 3 reports average deposition rates for the entire year and for the snowfall season (November-March), and also expresses these deposition rates as composite concentrations (total deposition divided by total amount of wet precipitation). These numbers are more suitable for comparisons with other years at the same site and with other sites than the individual weekly values.

Chemistry of Fresh Snow

Fresh snow was sampled immediately after snowfall on 11 dates between early November and late March. The data are summarized in Table 4. In addition, Table 5 provides a comparison of the composite average concentration of constituents in fresh snow with the composite average concentrations in bulk precipitation for the entire year and for the snowfall season.

As shown by Table 4, the depths of snow ranged between 2.1 cm and 30 cm. Snow densities were slightly higher earlier and later in the season than in the middle of the season, but the trend is not of great magnitude. The pH of new snow was of the range that might be expected on the basis of the data for bulk precipitation. The median pH value (4.9) was slightly lower than for

bulk precipitation, as would be expected given that bulk precipitation includes dry deposition, which is likely to contain a higher proportion of alkaline materials.

Table 4 suggests a negative relationship between the amount of snow, expressed as water equivalent, and the concentrations of dissolved substances. Conductance, which can be taken as a good general indicator of the total concentration of ionic solids, was tested by means of linear regression for inverse relationship with precipitation volume. The relationship, although not quite significant at the 5% level ($P = 0.056$), is highly suggestive; a somewhat larger data base would be very likely to show significance at the 5% level. Linear regression also is suggestive of inverse relationships between concentration of nitrate or sulfate and the amount of snow: for nitrate, $P = 0.08$ and for sulfate $P = 0.14$.

The snow surfaces in the collections made between November and the middle of December consistently showed temperature gradient metamorphism (Type III), and were typically of sub-type A, indicating early metamorphosis according to the classification of Sommerfeld (1976). Subsequent to the middle of December, there were incidences of unmetamorphosed snow (Type I) and of Type II snow (equitemperature metamorphism). Unmetamorphosed snow is coded in Table 4 according to the classification of Mongono and Lee (1968).

Deposition on the Snow Surface

Deposition on the snow surface after snowfall was determined directly by measurements of the amount of given chemical constituents per unit area in the snow just after snowfall and at the end of a snow sampling interval. The snow sampling intervals varied in duration from 2-4 days. These estimates,

expressed as $\text{mass/m}^2/\text{wk}$, are shown in the top row of Table 6. For chloride, sodium, and potassium, the deposition was too small to be differentiated from zero. However, for sulfate and nitrate, which are of principal interest, estimates were possible. In addition, estimates were possible for calcium, magnesium, and ammonium.

A second, and independent, estimate of the deposition to the snow surface is possible by calculation of the difference between bulk deposition and the composite average of chemical composition in new snow (Table 5). Since the measurements in this case are more numerous, estimates are possible for all of the variables listed in Table 6. The estimates for sulfate and nitrate agree very well with those obtained by the other method. Estimates for ammonium also agree reasonably well, as do those for magnesium. For reasons that are not evident, the two estimates for calcium are not in very good agreement.

The bottom line in Table 6 lists the mean estimated deposition of atmospheric materials to a snow surface once a snow cover has been established. Table 7 puts these deposition rates into perspective by comparison with total annual deposition and with total winter deposition. Table 7 shows that the percentage of all constituents deposited in winter is less than 50% of the total annual deposition. Of the deposition that occurs in winter, the proportion that occurs in the form of snow exceeds the proportion that occurs as dry deposition to the snow surface for ammonia, chloride, nitrate, and potassium. The two sources of deposition are almost equally balanced for calcium and sodium. Dry deposition to the snow surface exceeds deposition in the form of snow for sulfate and magnesium. The last two rows of Table 7 show the annual deposition to the snow surface both in

absolute and relative terms. In no instance does the dry deposition to the snow surface exceed 20% of annual total deposition.

Air Extractions

Air extractions were successfully completed over 11 different time intervals during the winter. For sulfur oxides, represented analytically by sulfate, the results of the extraction can be grouped into three categories: dates on which the amount extracted was indistinguishable from zero, dates on which the amount extracted was distinguishable from zero but measurements could be considered only approximate (one significant figure), and dates on which the amount extracted was sufficiently high to yield a good measurement (two significant figures). Two of the extractions fell in the first category, 7 in the second category, and 2 in the third category. The two extractions that yielded the highest concentrations serve as the best basis for estimating the capture efficiency of the extraction device for sulfur oxides. In each case, the amount of sulfate in the first extraction tube was far greater than that in the second extraction tube, and the difference between the second and the third extraction tube was so small that it was non-measurable. For the extraction of 23 February, the amount of sulfate in the first tube was 11.5 ug and the amount in the second tube was 0.3 ug. This indicates that the first tube contained over 95% and the first two tubes over 99% of the sulfur oxides that could be extracted in the form of sulfate. For the extraction beginning on 13 March, sulfate was 18.3 ug in the first tube and 1.8 ug in the second. This also suggests that 90% of the extractable sulfur oxides in the first tube and 99% in the first two tubes. If all of the extractions except the two for which the sulfate was actually undetectable in the first tube are pooled,

we obtain a total of 52 ug for tube 1 and 8 ug for tube 2. This suggests 84% recovery of the sulfate in the first tube. Thus all of the data together indicate close to 90% (± 5%) recovery of sulfate in the first tube. For calculation purposes, we shall use 90% recovery in the first tube.

Using the 90% extraction estimate for the first tube in each extraction series except the two in which there was no detectable sulfate, we obtain estimates of sulfur in the atmosphere as shown in Table 8. The results are expressed on volume basis, assuming that the combined effects of temperature and pressure at the site cause the volume of one mole of gas to be equal to only 70% of its volume at standard temperature and pressure, or 15.7 liters.

For nitrogen oxides, both nitrite and nitrate were analyzed, but nitrite was always present in much smaller quantities than nitrate and was therefore disregarded. For nitrate, 4 of the 11 extractions produced amounts indistinguishable from zero. Seven extractions produced amounts of nitrate in tube 1 that could be measured with moderate confidence (one significant figure), and none of the extractions produced amounts of nitrate that could be measured with high confidence. For the extractions interpretable with moderate confidence, the summation of the amounts of nitrate in tube 1 yielded 10.6 ug (as N), whereas a summation of the amounts of nitrate in tube 2 was 0.9 ug. On this basis, it appears that the extractable nitrogen oxides are 90% found in tube 1. On this basis, the contents of tube 1 have been converted to atmospheric concentrations as shown in Table 8.

Sedimentation Velocities

Given information on the concentration of a certain constituent in the atmosphere and the observed accumulation of this material on a snow surface

over the same interval, it is possible to compute sedimentation velocities for the interval. However, the computations for individual sampling intervals in this instance are not justifiable because of the propagation of random errors. For confident computation of individual sedimentation velocities, which involves division of one estimate by another, both the atmospheric concentrations and the accumulation rates should be known to at least two significant figures. In the present instance, both estimates can be specified to one significant figure, and only occasionally to two significant figures. Thus the calculation of deposition velocities for individual dates cannot be justified. It is justifiable, however, to compute an average deposition velocity based on average atmospheric concentrations and average rates of accumulation on dry snow surfaces over the course of the entire snow season; in this case error propagation is greatly reduced by the use of means. Table 8 reports the results of such calculations for both nitrogen and sulfur oxides. For nitrogen oxides, the mean sedimentation velocity over the entire snow season during dry weather was 1.0 cm/sec, and the sedimentation for nitrogen oxides under the same conditions was 0.76 cm/sec.

Discussion

The bulk deposition over the study year was very similar to the bulk deposition documented for previous years (Lewis et al. 1984, Grant and Lewis 1982). For example, Lewis et al. reported $5.2 \text{ mg/m}^2/\text{wk}$ as calcium deposition in 1982-83, and the deposition for the study interval was $5.6 \text{ mg/m}^2/\text{yr}$. Sulfate deposition in 1982-83 was $24 \text{ mg/m}^2/\text{yr}$ and in the present study it was $25 \text{ mg/m}^2/\text{yr}$. Nitrate nitrogen deposition was $3.9 \text{ mg/m}^2/\text{wk}$ in 1982-83 and $4.5 \text{ mg/m}^2/\text{wk}$ in the present study.

Composite average concentrations for bulk deposition in the snow season and over the whole year show that the bulk deposition during winter for all constituents except calcium, which is essentially the same for both seasons, is lower than it is the rest of the year. This is partly explained by the larger amount of wet precipitation occurring during the warm season. Other factors, including seasonal changes in the likelihood of upslope air movement, may also be involved, however.

The lower concentration of all substances in new snow than in bulk deposition during the snow season is expected on the basis of the contributions of dry deposition to the bulk deposition. The difference is very large for constituents that are strongly affected by dry deposition, including most notably calcium. Sulfate shows a surprisingly large difference between new snow and bulk deposition, indicating substantial dry deposition of sulfate, as confirmed by calculations of deposition onto the snow surface as shown in Tables 6 and 7.

Several lines of evidence indicate that the extraction device used in this study has considerable potential for further work. The greatest merit of the device is that it provides a composite estimate of all fractions of sulfur and nitrogen oxides without the use of separate techniques to measure each of the fractions in the gas phase. While knowledge of the concentrations of the individual fractions is of great use in connection with studies of atmospheric chemistry proper, ecologically oriented studies of deposition may actually be handicapped by such complexity. Furthermore, it is useful to have a device that can make an extraction over a period of several days so that repeated instantaneous measurements are not necessary.

The separate chemical species that make up sulfur and nitrogen oxides in the atmosphere have different solubilities. Thus it was not a foregone conclusion that the extraction procedure would have a high efficiency. However, on the basis of the high proportion of both sulfur and nitrogen oxides found in the first of four extraction tubes, it appears that the sulfur and nitrogen oxides in the atmosphere at this site were very efficiently extracted by the water extraction technique. In fact, the results suggest that the use of more than one or two tubes may be entirely unnecessary, although detailed studies of the extraction efficiency with individual chemical species would be desirable before this conclusion is reached with certainty.

Also indicative of the successful performance of the extraction apparatus are the final estimates of deposition velocities. For sulfur oxides, the final average estimate for the winter season is 1.0 cm/sec. Deposition velocities of this magnitude are typically assumed for sulfur oxides (e.g., Davis 1983). The extractor, of course, does not distinguish between sulfate and gaseous sulfur dioxide. Fehsenfeld and colleagues (personal communication), who have studied the gas phase oxides near the study site, have found sulfur dioxide present at concentrations between 5 ppt and 5 ppb, with an average of about 100 ppt. It is expected that the amount of sulfate would be of the same order of magnitude (e.g., Barrie et al. 1984). Thus the total expected sulfur oxide concentrations would average, on the basis of experience of the Fehsenfeld group, about 200 ppt by volume, which compares very well with the measured average in this study (255 pptv).

The computed average sedimentation velocity for nitrogen oxides in this study, 0.76 cm/sec, also falls within the expected range (McRae and Russell

1984). For the site, Fehsenfeld and colleagues report NO_x of 60 ppt to 20 ppb and an average of about 300 ppt. In addition, there is nitric acid and some PAN. Thus the observed average of 209 pptv for the present study is very close to the range expected as an average on the basis of direct gas phase measurements by Fehsenfeld and colleagues.

The greatest shortcoming of the extraction device used in this study was that it could not produce sufficiently high concentrations of oxides in water to be measured in the aqueous phase at two to three significant figures, as would be required for event-based calculation of deposition velocities rather than average deposition velocities over the entire season. This shortcoming is due entirely to the fact that the design of the extractor leads to an upper limit on the passage of air through the extraction tube in the vicinity of 800 ml/min. This in turn means that the amount of material in the tube at the end of the three-day extraction will often be below 5 ug, and sometimes even below 1 ug. The ion chromatograph configuration used in the analysis could not provide estimates of the concentrations of sulfur oxides in this range to more than one significant figure.

There are two obvious kinds of improvements that could be made in the use of the extractor to allow the estimation of sedimentation velocities on an event basis. First, the volume of air passing through the extraction tube could be increased by an alternate design for the extractor. Although it is likely that the tubes could be redesigned in this manner, mere changes in dimensions or in the force of the vacuum would not necessarily be effective, as experience with the tubes showed that passage of air through fine holes as necessary to break up the air train entering the system was impractical above a certain air flow. Enlargement of the intake or the diffuser plate merely

enlarges the amount of water that must be loaded with soluble substance in order to be analyzed and thus does not solve the problem. However, it is possible that a more complex designed could achieve the desired purpose.

Another possible step that could be taken to improve the accuracy of individual measurements for extraction would be reconfiguration of the ion chromatograph. More extensive use of the concentration capabilities of the ion chromatograph would be possible, for example. There is, however, another kind of difficulty that becomes apparent when ions are concentrated from large volumes. As noted in the methods section, field blanks are held side-by-side with the functioning extraction tubes. At the very lowest concentrations, the amounts of the substances of interest in the field blanks are by no means trivial. Consequently, subtraction of these blanks from the experimental tubes results in statistical noise that strongly affects the reliability of any given measurement. Although even greater precautions could be taken to maintain absolute purity of the sampling equipment and deionized water, precautions beyond a certain level for field instrumentation are not practical. Hence, a more satisfactory solution would be the extraction of a larger volume of air in the same volume of water, which would obviate difficulties with the blank.

Improvements in the computation of sedimentation velocity on the basis of the extractor data must also take into account the confidence with which accumulated dry deposition on a natural snow surface can be documented. The amount of effort that was required to isolate extraction intervals 3-4 days long during which a natural snow cover would remain undisturbed either by significant additional new snow, temperatures warm enough to melt existing snow, or wind sufficient to disturb the snow surface was very great. Thus the

possibility of extending the interval over which dry deposition could occur is probably impractical without some modification of the snow collector.

Conceivably, the snow collector could be shielded from the top to prevent the influence of additional snowfall or could be shielded from the sides to prevent disturbance by wind. However, neither of these alternatives is very desirable in view of the interference with natural air flow and deposition processes. Without a more extended interval over which deposition can occur, a subsampling of the snow is subject to sufficient variation, even without the action of wind, additional snow, or melting, to limit the confidence in the amount of the substance per unit area to two significant figures, whereas three would be preferable. On the other hand, more elaborate control over the environmental conditions surrounding the snow surface would introduce a lack of realism. It is evident from these considerations why so few empirical measurements have been made of deposition on specific environmental surfaces.

Our studies of the snow surface at the Como Creek watershed lead to the conclusion that the deposition of oxides, and especially of sulfur oxides, occurs in significant amounts to dry surfaces by the mechanism of dry deposition during the winter. Furthermore, by estimation of seasonal averages for sedimentation velocities, the study provides a vehicle for the computation of the effects of increases in the atmospheric burden of sulfur and nitrogen oxides at this and other similar sites.

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Figure Captions

Figure 1. Location map showing the Como Creek study site.

Figure 2. Design of the bulk collector (from Lewis and Grant 1978).

Figure 3. Design of the extraction tubes used in the air sampling portion of the program.

A map of Colorado showing the location of the study area. The map highlights Rocky Mountain National Park, Estes Park, Grand Lake, Ward, Nederland, Boulder, and Denver. A scale bar indicates 0 to 50 miles. An inset map shows the location of the study area within the state of Colorado.

CROSS SECTION

18"

1/4" PLEXIGLAS

WOODEN SUPPORTS AND BRACES

POLYPROPYLENE FUNNEL

TUBING

LOOP

MAIN VESSEL

OVERFLOW VESSEL

LIGHT BULB

1" STYROFOAM INSULATION

3/8" PLYWOOD

70 WATT POWER SOURCE

30"

30"

THERMOSTAT

RING STAND

Fig. 2. Schematic diagram of bulk precipitation collector (see text).

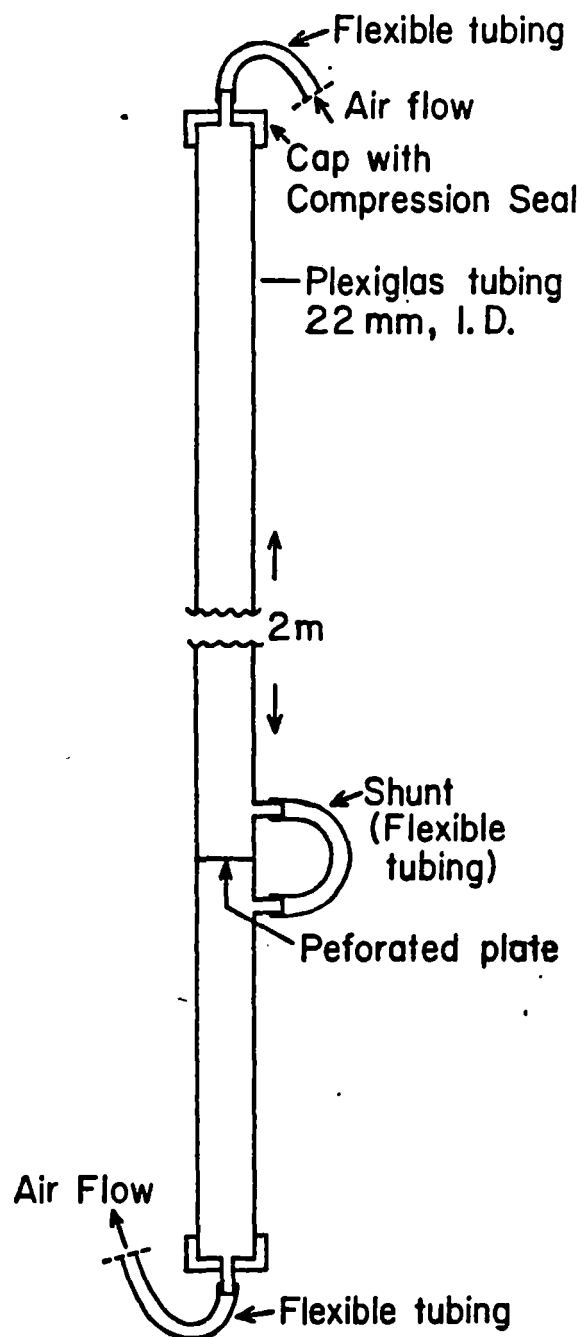


Figure 3. Diagram of one of the extraction tubes

1. Physical and chemical characteristics of bulk precipitation.

ID#	DATE	VOLUME liters	DILUTION R2+D1/R2	pH on Diluted sample? 1=yes	pH	COND umho/cm	XP	PARTIC ppm	SRP ppb	TDP ppb	TPP ppb	NO2-N ppb	NH4-N ppb
472	03-Jul-84	0.610	NA		5.4	20.9	NA	NA	NA	NA	NA	NA	NA
473	11-Jul-84	3.070	1.15		5.4	9.3	0.16	87.83	17.50	48.37	159.92	31.48	33.06
474	18-Jul-84	3.135	1.15		5.2	12.4	0.03	12.00	21.69	29.20	4.13	5.08	NA
475	25-Jul-84	3.790	1.10		4.7	17.7	0.12	10.02	9.69	21.68	27.37	5.88	515.85
476	01-Aug-84	13.000	1.12		4.6	12.7	0.19	6.56	2.00	5.70	14.12	3.81	418.56
477	08-Aug-84	3.620	1.14		4.7	10.8	0.91	2.01	6.76	11.16	20.82	4.26	97.69
478	15-Aug-84	6.130	1.08		4.9	12.1	0.18	6.45	0.33	3.83	12.60	1.67	327.81
479	22-Aug-84	4.800	1.10		4.5	12.5	0.21	4.40	0.65	3.27	10.38	2.02	142.53
480	29-Aug-84	3.150	1.17		4.3	14.9	0.13	5.47	3.13	7.32	8.54	2.48	206.55
481	05-Sep-84	1.100	1.52		5.3	12.9	0.22	13.21	25.87	39.70	43.87	1.63	246.21
482	11-Sep-84	3.860	1.13		5.2	8.5	0.26	7.34	3.01	11.32	21.42	4.01	113.11
483	16-Sep-84	1.830	1.47		5.6	12.3	0.19	10.69	25.74	34.51	29.77	17.36	162.75
484	25-Sep-84	1.000	1.60		5.4	16.4	0.14	27.54	57.54	57.57	60.09	5.84	582.89
485	02-Oct-84	3.380	1.15		4.8	14.5	0.21	6.98	11.91	15.87	16.72	7.21	476.50
486	09-Oct-84	6.140	1.09		4.6	29.4	0.07	7.09	4.51	5.82	5.66	4.02	321.38
487	17-Oct-84	3.500	1.00		4.3	24.6	0.12	4.09	13.76	15.94	4.96	2.11	1257.62
488	23-Oct-84	3.330	1.18		5.0	9.0	0.10	14.75	5.15	15.34	17.44	3.94	211.47
489	30-Oct-84	1.260	1.15		4.5	10.4	0.06	15.05	0.51	3.68	10.82	6.06	177.21
490	06-Nov-84	1.040	1.55		4.9	15.7	0.09	20.00	6.21	11.99	28.53	3.00	289.02
491	13-Nov-84	2.290	1.23		5.3	4.5	0.14	7.97	0.64	3.24	13.81	3.27	55.49
492	20-Nov-84	1.865	1.29		4.9	8.0	0.11	6.14	0.00	2.34	8.59	1.85	102.13
493	26-Nov-84	0.010	100.00		NA	NA	0.06	7.18	23.70	320.00	426.00	57.00	3803.37
494	04-Dec-84	0.380	2.04		5.0	12.9	0.16	14.43	1.66	6.48	48.11	4.67	97.53
495	10-Dec-84	0.020	44.50	1	5.7	3.6	0.09	13.11	79.20	127.72	541.12	17.36	297.26
496	17-Dec-84	5.480	1.04		5.0	4.9	0.19	3.53	0.00	1.63	6.89	0.75	11.50
499	08-Jan-85	0.870	1.67		4.8	8.4	0.06	14.41	1.23	10.40	13.69	2.33	46.94
500	14-Jan-85	0.020	50.00	1	5.7	4.1	0.08	2.12	59.00	65.71	89.00	48.36	2569.45
501	22-Jan-85	1.485	1.72	1	4.8	6.7	0.30	1.94	2.54	5.21	9.37	2.27	98.60
502	28-Jan-85	0.315	3.77		4.3	22.7	0.07	9.98	0.00	2.15	27.45	7.26	122.60
503	04-Feb-85	0.450	2.86		4.7	13.3	0.15	7.46	0.00	6.80	32.49	19.54	884.29
504	11-Feb-85	0.465	2.60		4.2	18.7	0.12	8.66	1.92	2.57	26.99	11.07	247.35
505	18-Feb-85	0.065	15.39		5.1	5.8	0.11	15.11	18.16	34.17	249.62	2.77	576.36
506	25-Feb-85	3.350	1.17		5.5	6.3	0.13	2.99	0.51	1.44	4.45	4.14	293.51
507	04-Mar-85	2.755	1.11		5.8	6.4	0.13	6.15	0.66	1.55	8.63	7.36	203.54
508	11-Mar-85	2.220	1.22		5.8	4.9	0.15	4.96	1.09	0.31	9.09	2.46	73.58
509	18-Mar-85	0.820	1.73		5.0	8.6	0.14	5.30	1.02	3.13	13.19	5.34	127.50
510	25-Mar-85	1.480	1.37		6.1	24.8	0.09	26.10	1.22	2.59	30.74	22.37	775.02
511	02-Apr-85	3.600	1.00		5.5	8.8	0.31	4.35	0.81	3.70	13.28	7.55	160.84
512	08-Apr-85	3.360	1.13		6.1	10.2	0.22	6.92	0.34	1.86	17.15	5.93	131.36
513	15-Apr-85	0.170	5.88	1	5.8	7.4	0.09	22.03	6.09	19.33	110.76	10.32	344.96
514	23-Apr-85	3.570	1.14		5.2	11.0	0.13	16.50	NA	NA	25.35	NA	NA
515	29-Apr-85	3.520	1.15		5.0	6.8	0.25	2.86	0.00	0.65	8.11	1.27	89.09
516	06-May-85	3.600	1.14		5.1	7.5	0.19	5.09	4.55	0.19	11.01	5.23	197.41
517	14-May-85	1.565	1.34		5.3	4.6	0.10	18.59	2.77	4.72	26.01	3.08	86.23
518	21-May-85	3.120	1.16	1	4.8	12.8	0.41	2.20	NA	2.00	10.35	6.12	306.31
519	28-May-85	2.840	1.16		4.3	25.3	0.06	6.10	0.86	4.38	4.08	3.43	571.18
520	04-Jun-85	3.220	1.14		5.1	13.0	0.14	12.86	2.70	3.43	20.25	3.87	262.65
521	11-Jun-85	0.765	1.67		5.9	22.6	0.20	21.82	5.19	63.76	72.09	9.89	546.62
522	18-Jun-85	0.920	1.58		5.7	11.7	NA	29.74	54.72	89.26	NA	52.54	23.32
523	24-Jun-85	0.380	2.97	1	5.6	NA	0.09	172.26	85.27	222.72	449.92	8.35	21.56

2. Chemical loading rates from bulk precipitation.

	PRECIP	H+	PARTIC	SRP	TDF	TPP	NO2-N	NH4-N	TDN	Si	Cl	NO3-N	SO4
	mm/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk	ug/m2/wk
472	3.5	0.01	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
473	13.3	0.05	1165.10	232.15	641.65	2121.41	417.60	438.82	4625.88	NA	5.41	182.40	20.03
474	15.5	0.10	185.78	335.79	452.06	63.94	78.65	NA	2767.79	NA	6.16	5844.41	22.22
475	18.7	0.37	187.44	181.36	405.76	512.26	110.05	9654.67	21982.30	NA	2.49	12184.77	42.49
476	64.2	1.61	421.14	128.40	365.93	906.47	244.59	26870.52	67376.80	10.27	6.10	24538.67	NA
477	17.9	0.36	35.93	120.85	199.50	372.19	76.15	1746.36	3874.87	0.89	1.02	6434.75	21.45
478	30.3	0.38	195.25	9.99	115.94	381.42	50.55	9923.03	32690.90	0.00	1.06	11652.72	60.00
479	23.7	0.75	104.30	15.41	77.51	246.04	47.88	3378.49	4473.38	1.07	NA	1116.44	NA
480	15.6	0.78	85.09	48.69	113.87	132.84	38.58	3213.00	10062.43	NA	NA	NA	NA
481	5.4	0.03	71.76	140.53	215.65	238.31	8.85	1337.44	4201.33	0.43	1.08	2185.77	10.73
482	22.2	0.14	163.32	66.94	251.74	476.35	89.18	2515.42	10441.80	0.00	2.40	3917.12	23.62
483	9.0	0.02	96.61	232.61	311.87	269.03	156.88	1470.78	NA	NA	0.34	2634.55	12.34
484	4.9	0.02	136.01	284.15	284.30	296.74	28.84	2878.47	13944.75	0.40	7.46	1892.64	13.23
485	16.7	0.26	116.51	196.79	264.89	279.08	120.34	7953.43	29710.41	0.85	4.04	8458.06	18.06
486	30.3	0.76	214.98	136.75	176.47	171.62	121.89	9744.56	29904.19	0.55	0.00	12222.57	41.45
487	15.1	0.76	61.85	208.10	241.07	75.01	31.91	19019.56	37405.29	0.86	0.58	23310.16	84.44
488	19.2	0.19	282.98	98.86	294.30	334.59	75.59	4057.09	16735.18	0.23	0.00	5526.06	19.93
489	6.2	0.20	93.64	3.17	22.90	67.32	37.71	1102.64	4388.85	0.01	0.15	2798.63	166.07
490	5.1	0.06	102.72	31.89	61.58	146.52	15.41	1484.35	4539.52	0.00	1.54	4203.94	18.32
491	11.3	0.06	90.14	7.24	36.64	156.17	36.98	627.52	3247.39	0.00	0.40	1170.70	8.38
492	9.2	0.12	56.55	0.00	21.55	79.11	17.04	940.60	3770.48	0.00	0.10	1675.70	12.97
493	0.1	NA	0.41	1.37	18.44	24.54	3.28	219.12	1126.22	0.86	0.00	93.01	152.93
494	1.6	0.02	23.69	2.72	10.64	79.00	7.67	160.14	801.51	NA	NA	NA	NA
495	0.1	.00	1.51	9.13	14.72	62.35	2.00	34.25	595.31	0.12	0.01	0.00	0.01
496	27.1	0.30	95.50	0.00	44.00	186.46	20.30	311.10	4692.08	0.22	NA	NA	NA
499	1.4	0.02	19.70	1.69	14.22	18.71	3.19	64.16	386.81	0.09	0.07	161.80	4.33
500	0.1	.00	0.24	6.89	7.57	10.26	5.57	296.07	1676.00	0.22	0.33	594.04	2.54
501	6.4	0.11	12.45	16.30	33.43	63.33	14.57	632.68	3401.86	0.19	0.06	2062.38	11.29
502	1.8	0.09	18.11	0.00	3.90	49.82	13.21	222.50	2047.04	0.15	0.42	1571.85	9.51
503	2.2	0.04	16.58	0.00	15.11	72.20	43.42	1965.09	3290.45	1.71	0.05	918.67	8.02
504	2.4	0.17	20.74	4.60	6.16	64.64	26.50	592.42	3695.99	3.23	1.18	2554.00	6.78
505	0.3	.00	4.85	5.83	10.97	80.12	0.89	185.00	1664.10	0.94	0.32	78.79	5.05
506	16.5	0.05	49.50	8.44	23.82	73.62	68.49	4855.60	10735.19	0.33	0.67	3656.71	12.42
507	13.6	0.02	87.67	8.98	21.09	117.41	100.13	2769.15	6262.17	0.27	1.50	2397.78	11.16
508	11.0	0.02	54.38	11.95	3.40	99.65	26.97	806.44	6760.72	2.08	1.35	2286.47	0.89
509	4.0	0.04	21.46	4.13	12.67	53.41	21.62	516.30	2144.19	0.28	0.89	1170.43	7.29
510	7.3	0.01	190.76	8.92	18.93	224.67	163.49	5664.34	11915.45	0.66	4.02	9790.73	21.34
511	15.6	0.05	67.67	12.60	57.56	206.58	117.44	2501.96	9282.86	0.40	1.40	5745.13	15.09
512	19.4	0.02	133.96	6.58	36.01	331.99	114.79	2542.87	9591.11	0.29	2.90	4282.58	34.84
513	0.8	.00	18.49	5.11	16.23	92.98	8.66	289.60	1399.38	0.18	0.64	613.25	4.94
514	15.4	0.10	254.53	NA	NA	391.05	NA	NA	NA	NA	2.62	4230.41	22.83
515	20.3	0.20	58.00	0.00	13.18	164.47	25.76	1806.73	7997.43	0.61	2.23	4921.31	15.62
516	17.8	0.14	90.49	80.89	3.38	195.73	92.98	3509.51	10359.77	NA	10.49	3153.42	13.33
517	6.8	0.03	125.71	18.73	31.92	175.89	20.83	583.12	2717.77	0.27	0.61	1124.04	5.27
518	15.4	0.24	33.90	NA	30.81	159.47	94.29	4719.44	19411.08	0.45	1.39	8956.79	41.60
519	14.0	0.79	85.55	12.06	61.43	57.22	48.10	8010.62	17188.66	0.74	1.49	8615.93	33.10
520	15.9	0.13	204.49	42.93	54.54	322.00	61.54	4494.48	14204.42	NA	2.86	8061.13	20.35
521	3.8	.00	82.43	19.61	240.87	272.34	37.36	2065.01	8713.96	0.64	2.00	3842.87	37.59
522	4.5	0.01	135.12	248.60	405.53	NA	238.70	105.95	3624.68	0.45	NA	NA	NA
523	2.2	0.01	377.13	186.68	487.60	985.01	18.28	47.20	246.16	NA	1.95	414.78	7.22

e 1. Physical and chemical characteristics of bulk precipitation. (continued).

IDB	TDN ppb	Si ppm	Cl ppm	NO3-N ppb	SO4 ppm	Na ppm	K ppm	Ca ppm	Mg ppm
472	NA	NA	NA	NA	NA	NA	NA	NA	NA
473	348.72	NA	0.41	13.8	1.51	0.42	0.58	0.57	0.17
474	178.78	NA	0.40	377.51	1.44	NA	NA	NA	NA
475	1174.52	NA	0.13	651.03	2.27	0.11	0.18	0.74	0.12
476	1049.52	0.16	0.10	382.24	NA	NA	0.10	0.37	0.08
477	216.76	0.05	0.06	359.96	1.20	0.00	0.05	0.21	0.04
478	1079.92	0.00	0.04	384.94	1.98	0.22	0.04	0.37	0.12
479	188.72	0.05	NA	47.10	NA	0.00	0.11	0.24	0.03
480	646.87	NA	NA	NA	NA	0.00	0.11	0.26	0.06
481	773.43	0.08	0.20	402.38	1.98	0.16	0.82	0.60	0.10
482	469.53	0.00	0.11	176.14	1.07	0.05	0.62	0.20	0.12
483	NA	NA	0.04	291.53	1.37	0.15	0.81	0.59	0.14
484	2823.81	0.08	1.51	381.24	2.68	0.69	2.00	1.05	0.20
485	1779.99	0.05	0.24	506.73	1.08	0.07	0.22	0.49	0.07
486	986.25	0.02	0.00	403.11	1.37	0.00	0.62	0.27	0.03
487	2473.33	0.06	0.04	1541.32	5.58	0.00	0.07	0.39	0.02
488	872.30	0.01	0.00	288.04	1.04	0.00	0.25	0.16	0.02
489	705.35	.00	0.02	449.78	26.69	8.56	0.11	0.19	0.03
490	883.90	0.00	0.30	818.56	3.57	0.32	0.22	2.62	0.13
491	287.16	0.00	0.04	103.52	0.74	0.00	0.06	0.30	0.02
492	409.39	0.00	0.01	181.95	1.41	0.00	0.01	0.41	0.03
493	19547.88	15.00	NA	1614.35	2654.50	1010.60	6.80	10.69	2.12
494	488.14	NA	NA	NA	NA	8.61	0.46	1.08	0.18
495	5166.41	1.02	0.06	0.00	0.13	1.83	4.60	5.67	0.93
496	173.38	0.01	NA	NA	NA	0.00	0.06	0.09	0.01
499	282.96	0.07	0.05	118.36	3.17	0.63	0.14	0.57	0.07
500	14545.26	1.95	2.88	5155.45	22.05	9.90	3.50	6.72	0.75
501	530.16	0.03	0.01	321.41	1.76	0.14	0.07	0.17	0.02
502	1127.96	0.08	0.23	866.12	5.24	0.32	0.15	0.44	0.01
503	1480.70	0.77	0.02	413.40	3.61	0.76	0.77	0.45	0.05
504	1543.17	1.35	0.49	1066.36	2.83	0.77	0.29	0.52	0.07
505	5184.32	2.92	1.00	245.46	15.74	2.86	2.46	2.14	0.34
506	648.92	0.02	0.04	221.04	0.75	0.17	0.05	0.07	0.01
507	460.29	0.02	0.11	176.24	0.82	0.18	0.08	0.27	0.01
508	616.69	0.19	0.12	208.56	0.08	0.20	0.07	0.56	0.05
509	529.51	0.07	0.22	289.04	1.80	0.36	0.24	0.78	0.09
510	1630.32	0.09	0.55	1339.61	2.92	0.48	0.16	2.15	0.21
511	596.76	0.03	0.09	369.33	0.97	0.18	0.07	0.64	0.06
512	495.46	0.02	0.15	221.23	1.80	0.37	0.08	0.96	0.10
513	1666.91	0.22	0.76	730.49	5.88	1.06	1.18	2.76	0.32
514	NA	NA	0.17	274.24	1.48	0.21	0.11	0.99	0.10
515	394.35	0.03	0.11	242.67	0.77	0.07	0.03	0.38	0.03
516	582.74	NA	0.59	177.38	0.75	0.13	0.11	0.34	0.03
517	401.90	0.04	0.09	166.22	0.78	0.09	0.04	0.31	0.04
518	1259.85	0.03	0.09	581.33	2.70	0.28	0.03	0.39	0.05
519	1225.60	0.05	0.11	614.34	2.36	0.12	0.19	0.42	0.05
520	893.29	NA	0.16	506.95	1.28	0.35	0.18	0.86	0.10
521	2306.64	0.17	0.53	1017.23	9.95	5.06	0.76	1.72	0.23
522	797.82	0.10	NA	NA	NA	0.24	0.60	0.95	0.16
523	112.44	NA	0.59	189.46	3.30	0.50	3.47	2.05	0.53

e 2. Chemical loading rates from bulk precipitation.(continued).

ID	Na	K	Ca	Mg
	mg/m2/wk	mg/m2/wk	mg/m2/wk	mg/m2/wk
472	NA	NA	NA	NA
473	5.57	7.69	7.56	2.26
474	NA	NA	NA	NA
475	2.10	3.35	13.76	2.28
476	NA	6.42	23.75	5.14
477	0.00	0.84	3.75	0.68
478	6.66	1.21	11.20	3.63
479	0.00	2.65	5.62	0.69
480	0.00	1.76	3.97	1.00
481	0.87	4.43	3.28	0.55
482	1.11	13.83	4.54	2.56
483	1.36	7.27	5.30	1.29
484	3.39	9.87	5.19	0.96
485	1.19	3.69	8.15	1.08
486	0.00	0.49	8.22	0.85
487	0.00	1.03	5.88	0.33
488	0.00	4.78	2.97	0.40
489	53.26	0.68	1.15	0.18
490	1.64	1.12	13.46	0.67
491	0.00	0.63	3.40	0.19
492	0.00	0.09	3.79	0.29
493	58.22	0.39	0.62	0.12
494	14.14	0.76	1.77	0.29
495	0.21	0.53	0.65	0.11
496	0.00	1.70	2.46	0.14
499	0.86	0.19	0.78	0.09
500	1.14	0.40	0.77	0.09
501	0.90	0.45	1.09	0.13
502	0.58	0.27	0.80	0.02
503	1.69	1.71	1.00	0.11
504	1.84	0.69	1.25	0.17
505	0.92	0.79	0.69	0.11
506	2.81	0.83	1.16	0.17
507	2.45	1.09	3.67	0.14
508	2.19	0.77	6.14	0.55
509	1.46	0.97	3.16	0.36
510	3.51	1.17	15.71	1.53
511	2.80	1.09	9.96	0.93
512	7.16	1.55	18.58	1.94
513	0.89	0.99	2.32	0.27
514	3.24	1.70	15.27	1.54
515	1.42	0.61	7.71	0.61
516	2.31	1.96	6.04	0.53
517	0.61	0.27	2.10	0.27
518	4.31	0.46	6.01	0.77
519	1.68	2.66	5.89	0.70
520	5.57	2.86	13.68	1.59
521	19.12	2.87	6.50	0.87
522	1.09	2.73	4.32	0.73
523	1.09	7.60	4.49	1.16

	Precip mm	H ⁺ ug	Partic mg	SRP ug	TDP ug	TPP ug	NO ₂ ⁻ -N ug	NH ₄ ⁺ -N ug	TDN ug	Si mg	Cl mg	NO ₃ ⁻ -N ug	SO ₄ ⁼ mg	Na ⁺ mg	K ⁺ mg	Ca ⁺⁺ mg	Mg ⁺⁺ mg
Bulk Deposition (per m ² per wk)																	
Annual	11.69	190	121.32	65.50	125.63	239.98	64.22	3233.79	9649.79	0.76	1.78	4543.87	24.67	4.55	2.25	5.62	0.82
Snow Season**	6.36	59	44.09	6.63	21.13	86.64	32.48	1135.32	3764.04	0.57	0.72	2022.79	15.85	4.50	0.73	3.36	0.29
Composite Concentrations* (per liter)																	
Annual	-	16.0	10.18	5.28	10.33	19.73	5.28	260.62	777.71	0.051	0.13	351.25	1.83	0.37	0.18	0.46	0.068
Snow Season**	-	9.0	6.93	1.04	3.32	13.62	5.11	178.48	591.74	0.085	0.10	289.09	2.27	0.71	0.11	0.53	.046

* mass/ water

**November through March

Table 3. Mean bulk deposition and composite concentrations over the study year.

Date	Depth cm	Type (surface)	Volume liters (H ₂ O)	Density mg/cc	pH	Cond. umho/cm	NH ₄ ⁺ -N ug/l	Cl ⁻ mg/l	SO ₄ ⁼ mg/l	NO ₃ ⁻ -N ug/l	Ca ⁺⁺ mg/l	Mg ⁺⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l
10-Nov-84	11.8	III A.1	1.096	0.65	5.4	4.84	72.58	0.08	0.06	97.14	0.16	0.02	0.21	0.10
15-Nov-84	10.0	III A.1	0.945	0.66	5.1	5.28	104.23	0.10	0.62	110.23	0.16	0.02	0.11	0.05
29-Nov-84	2.1	III A.2	0.157	0.51	4.6	10.92	NA	0.20	NA	156.27	0.17	0.02	NA	0.14
14-Dec-84	26.3	III A.3	1.850	0.49	5.6	3.39	52.55	0.02	0.61	62.83	0.00	0.01	0.27	0.01
17-Dec-84	2.7	III A.1	0.185	0.48	4.8	6.97	126.30	0.30	1.02	217.26	NA	NA	NA	NA
11-Jan-85	8.0	I	0.520	0.45	4.8	6.48	94.07	0.57	0.39	114.26	0.10	.00	0.11	0.04
		(a)												
22-Jan-85	25.7	I	1.851	0.50	4.8	5.49	85.36	0.00	0.80	124.70	0.00	0.00	0.09	0.01
11-Feb-85	5.6	IIA.1,	0.420	0.52	4.2	14.79	221.23	0.25	1.27	643.40	0.07	0.00	0.09	0.06
		(b)												
		(c)												
23-Feb-85	30.2	I	1.550	0.36	5.3	5.52	203.96	0.04	0.58	164.13	0.02	0.00	0.57	0.44
13-Mar-85	6.9	IIA.1,	0.398	0.40	4.9	32.13	130.36	0.11	0.50	505.08	-	-	4.70	-
		(d)												
30-Mar-85	24.8	IIA.1,	1.797	0.51	5.5	5.69	244.46	0.05	0.25	2.7.77	-	-	0.05	-
		(e)												

(a) P.1F S1

(b) P1.C, P2.a

(c) P7.a, P1.f, CP1.b, P1.e

(d) P2a, G2, CP1.b

(e) P1.b, P1.e, CP1.b

Table 4. Chemistry of fresh snow.

	$\text{NH}_4^+\text{-N}$ ug/l	Cl^- mg/l	SO_4^{2-} mg/l	$\text{NO}_3^-\text{-N}$ ug/l	Ca^{++} mg/l	Mg^{++} mg/l	Na^+ mg/l	K^+ mg/l
New Snow	132	0.08	0.60	167	0.06	0.01	0.38	0.11
Bulk Deposition (Annual)	260	0.13	1.83	351	0.46	0.07	0.37	0.18
Bulk Deposition (Snow Season)	178	0.10	2.27	289	0.53	0.05	0.71	0.11

Table 5. Composite concentrations of selected constituents in new snow and bulk deposition.

	NH ₄ ⁺ -N ug	Cl ⁻ mg	SO ₄ ⁼ mg	NO ₃ ⁻ -N ug	Ca ⁺⁺ mg	Mg ⁺⁺ mg	Na ⁺ mg	K ⁺ mg
Deposition on Snow Surface During Sampling Periods (per m ² per wk)								
539	ND	9.3	93.3	0.43	0.14	ND	ND	
Deposition on Snow Surface Calculated by Difference (per m ² per wk)								
293	0.13	10.6	775	2.99	0.25	2.10	0.00	
Mean (per m ² per week)	416	0.13	9.9	854	1.71	0.20	2.10	0.00

*ND = not distinguishable from zero

Table 6. Deposition of dry atmosphere to the snow surface computed by two independent methods.

	NH_4^+-N	Cl^-	SO_4^{--}	NO_3^--N	Ca^{++}	Mg^{++}	Na^+	K^+
Total Annual Deposition (kg/ha/yr)	1.68	0.93	12.8	2.36	2.9	0.43	2.37	1.17
Percent Deposited in Winter (Nov-March)	15	17	27	19	25	15	41	14
Percent of Winter Deposits as Dry Deposition to Snow Surface	37	18	63	42	51	67	47	0
Percent of Annual Deposits as Dry Deposition to Snow Surface	5.5	3.1	17.0	8.0	12.8	10.0	19.3	0.0
Annual Dry Deposition to Snow Surface (kg/ha/yr)	0.09	0.03	3.18	0.19	0.37	0.04	0.46	0.0

Table 7. Deposition components for the year.

Sampling Interval (start)	Sulfur Oxides			Nitrogen Oxides		
	Confidence Category*	Sulfur pptv	Sulfate ug/m ³	Confidence Category*	Nitrogen pptv	Nitrogen ug/m ³
10-Nov-84	3	---	---	3	---	---
15-Nov-84	2	448	43.0	2	172	2.41
29-Nov-84	2	31	2.98	2	94	1.32
14-Dec-84	2	79	7.58	3	---	---
17-Dec-84	2	50	4.80	3	---	---
11-Jan-85	2	399	38.3	2	204	2.86
22-Jan-85	2	115	11.0	3	---	---
11-Feb-85	3	---	---	2	147	2.06
23-Feb-85	1	491	47.1	2	351	4.91
13-Mar-85	1	588	56.4	2	286	4.00
30-Mar-85	2	99	9.50	3	---	---
mean	---	255	24.4	---	209	2.93
mean Sedimentation Velocity (cm/s)		1.0	---	---	0.76	---

1 = good confidence, 2 = moderate, 3 = low; see text.

Table 8. Amounts of sulfur and nitrogen oxides in the air over the 11 sampling intervals.